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Fourth Semiannual Report on

NASA Grant NGR-40-002-026

PHOTOVOLTAIC EFFECT AND UTILIZATION OF PHOTOVOLTAIC CELLS

(Subtitle: Effects of Low Energy Electron Irradiation on Si Cells)

N67-32178 (ACCESSION NUMBER) 24 (PAGES) 1 (THRU) 86918 (NASA CR OR TMX OR AD NUMBER) 03 (CODE) (CATEGORY)

FACILITY FORM 602

January 1, 1967 to June 30, 1967

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Sponsored by: National Aeronautics and Space Administration
Office of Space Science Applications
Washington, D. C. 20546

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

July 1967

ABSTRACT

The effects of 115 keV electron irradiation on the short circuit current I_{sc} produced in silicon photovoltaic cells by strongly absorbed light ($\alpha \sim 10^5 cm^{-1}$) has been studied in the organic-vapor free vacua provided by a Vac-Ion pumping system. It is shown that the behavior of I_{sc} (and by inference, of surface recombination velocity) is a function of the resistivity of the bulk material whose surface is being irradiated. The resistivities investigated include 20 ohm-cm p-Si and 1, 20 and 50 ohm-cm n-Si. It is shown that irradiation in an organic-vapor free vacuum of 10^{-8} mm Hg by about 10^{15} electrons/cm^2 leads to a surface which is stable for long periods (about 20 hours) of time in contrast to the situation associated with irradiation in organic-vapor contaminated ambients where changes in I_{sc} begin to occur as soon as the electron beam is interrupted.

I. Introduction

In earlier reports[1] we discussed the concepts underlying the experimental technique which we have adopted to study how irradiation by electrons whose energy is too low to cause bulk defects affects the surface recombination velocity of germanium and silicon. The experiment involves measurement of the changes in the short circuit current I_{sc} of a photovoltaic cell illuminated by strongly absorbed light. It can be shown that I_{sc}^{-1} is a linear function of surface recombination velocity s in the case of excitation by such strongly absorbed light, so that one can relate changes in I_{sc} to changes in s. However, as has been pointed out, the technique suffers from the disadvantage that one cannot measure absolute values of s; only changes can be measured.

Most of our earlier experiments were performed in the vacuum produced by the diffusion pumps and cold traps of the Van de Graaff machine and there was always the possibility that the residual organic vapors in this vacuum played a role in the behavior of I_{sc} during the course of irradiation. Some of our earlier experiments were therefore performed in the vacuum produced by a Vac-Ion pump. However, the vacuum chamber in which those experiments took place was fitted with Neoprene gaskets and the possibility that residual organic vapors might contribute to the effects was still open. Consequently, even though experiments involving a comparison of the behavior of Ge photovoltaic cells irradiated in these two different systems did not result in any striking differences of behavior, we still had reservations concerning whether we had in fact eliminated organic vapors from the chamber used with the Vac-Ion pump. All irradiation of Si cells reported to date had been performed in the Van de Graaff vacuum and we reserved any decisions concerning effects of organic vapors until experiments could be performed in a vacuum system from which organic contaminants had been completely excluded. It is the purpose of this report to describe the effects of sub-threshold electron irradiation on surfaces of single crystals of both n- and p-Si of a few different resistivities for the case of the Si surfaces in contact with an organic-vapor free ambient and for the case of the Si surfaces in contact with the organic-vapor containing vacuum of the Van de Graaff machine. As we shall show, there are substantial differences in the behavior of the surfaces in these two situations.

II. Description of the Samples

The cells used in these experiments were the same ones used in the experiments described in our last interim report. They had been fabricated by diffusing an appropriate impurity (boron into n-Si and phosphorus into p-Si) into wafers of various initial resistivities. To date, four different base resistivities have been investigated, namely, 20 ohm-cm p-Si and 1 ohm-cm, 20 ohm-cm and 50 ohm-cm n-Si. The surface studied in these experiments was that opposite the diffused face. As described in our Third Semiannual Report, the distance between the irradiated surface and the p-n junction was less than a diffusion length which guaranteed that the inverse relation between I_{sc} and s would be satisfied.

The samples were mounted on Al_2O_3 wafers with GE cement. The Al_2O_3 wafers were attached to the copper cold finger of the sample mount. The Al_2O_3 provided electrical isolation from, and thermal contact with the copper cold finger, so that amount of electrons incident on the sample could be established by measuring the current absorbed in the samples.

III. Description of the Apparatus

Figure 1 is a schematic representation of the apparatus used to provide the organic-vapour free vacuum. The main body of the irradiation chamber is glass. There are three glass-metal seals, two of copper and one of Kovar. One of these seals (the one involving Kovar) leads to a fitting which matches the 4" output flange of a 75 l/sec Vac-Ion pump. A copper gasket seals the irradiation chamber to the pump via this flange. A second seal provides a place to mount a thin Ni (.0001") window over a 1" dia hole. The window is soldered in place and it provides isolation between the vacuum system produced by the Van de Graaff machine and that produced by the Vac-Ion pump. In addition, the window admits electrons accelerated by the Van de Graaff into the irradiation chamber. The copper sleeve which serves as a mount for the Ni window also provides a means for coupling the irradiation chamber to the Van de Graaff via the Veeco "quick" vacuum coupler as shown in the diagram.

The third glass to copper seal (not visible in Figure 1) provides a means for introducing the dewar(on whose copper cold finger the samples are mounted)into the system. The dewar is fitted with a mating copper sleeve and the two are soldered together. Thus we have eliminated all possible sources of organic vapours from the chamber. The seals were either copper gaskets or soldered joints.

The chamber was also fitted with a pyrex glass window through which light could be directed onto the sample. There are also Kovar fitting for admitting the required wires into the system for thermocouples and sample leads.

IV. Experimental Procedure

Before they were sealed into the new irradiation chamber, the surface of the cell which was going to be irradiated was washed successively in acetone and methanol. The Sorption Pumps were turned on and the irradiation chamber was heated to 100°C by heating tapes. This temperature was maintained even after the Vac-Ion pump was turned on until the pressure had dropped to the working level of about 10^{-8} mm Hg. Thus the whole system including the samples was kept at this elevated temperature for at least a few hours.

The cells were illuminated by the 3650Å line selected from the output of a Hg lamp with the help of a Kodak 18A filter. The absorption constant α for this light is about 2×10^5 cm^{-1}, i.e. the light is absorbed within 0.05μ of the surface and the resulting short circuit current is extremely sensitive to the electronic properties of the surface. All the measurements reported here were made with constant illumination, i.e., the light was not modulated. The light

intensity was monitored by a silicon photovoltaic cell external to the irradiation chamber in order to assure that it did not change during the experiment. A load resistance of 100Ω was connected across the sample and the signal was, therefore, proportional to the short circuit current I_{sc}. In our presentation of the data, we have chosen to plot V_{sc}, the voltage across the 100Ω series resistor. Since the magnitude of V_{sc} lay between 0.1 and 3.0 mV, V_{sc} was always directly proportional to I_{sc}.

The temperature of the cells was monitored during irradiation. It remained at 20°C ± 0.5°C at all times. Thus neither the electron beam power nor optical power to the sample was sufficient to cause any temperature rise. Consequently, the possibility of temperature effects need not be considered further.

The current received by the sample which was insulated electrically by the Al_2O_3 was fed to an Elcor Current integrator and the integrated flux to the sample was measured in this way. No corrections for reflection or transmission losses have been made. The beam current I_B varied between 0.05 and 0.3μA/cm^2.

The experiments proceeded as follows. The sample was exposed to the 3650Å light for a period of one hour until it was evident that the value of I_{sc} had stabilized. The Van de Graaff was then turned on and after an integrated flux of 50μ coul, the electron beam was interrupted by a solenoid operated shutter and the new value of I_{sc} was determined in the course of a minute or two. The irradiation was then resumed for another 50μ coul, etc. After the sample had accumulated an integrated flux of 1000μ coul, the radiation was stopped. The sample was allowed to rest for a period of about 20 hours and the irradiation was resumed according the the pattern described above.

Next the Vac-Ion pump was turned off and an amount of dry nitrogen sufficient to increase the pressure to about 10^{-3} mm Hg was admitted into the irradiation chamber.

The value of I_{sc} was followed during the period when the pressure was increasing. Then the sample was subjected to irradiation in this 10^{-3} dry N_2 ambient (which of course was also organic-vapour free). The irradiation procedure was like that outlined above. After delivery of about 1000μ coul to the sample, it was again allowed to rest for about 20 hours and the irradiation was repeated.

Finally the sample was removed from the chamber attached to the Vac-Ion pump and remounted in the chamber used for irradiations in the Van de Graaff vacuum. Before mounting, the sample was washed with acetone and then with methanol. Once the base pressure of about 10^{-5} mm Hg had been achieved in this system, the sample irradiation proceeded as described for the other vacuum conditions.

V. Experimental Results

In general, there were substantial differences between the changes induced in the course of the first irradiation of a freshly cleaned surface and the results of subsequent irradiations. Consequently the data is plotted in such a way as to display the results of the first irradiation and of the second and subsequent ir-

radiations. These subsequent irradiations produced essentially the same results as the second one. In all cases the electron energy was 115 keV.

Figure 2 shows the dependence of V_{sc} for the surface of p-Si, ρ = 20Ω cm in the Vac-Ion pump pressure of 10^{-8} mm Hg. The first irradiation produced an increase by a factor greater than 2 in V_{sc} (caused by a decrease in s by a similar factor) followed by saturation after about 500μ coul. The sample rested for about 20 hours after which time curve b was recorded. Note that there was very little change in V_{sc} during the 20 hour period between irradiations. Further note that resumption of irradiation returned V_{sc} to a value nearly equal to its initial value.

At this point dry N_2 was admitted to the system until the pressure reached 5×10^{-3} mm Hg. The curves shown in Figure 3 were then obtained. First of all, note that the increase in N_2 pressure led to a decrease in V_{sc}. Irradiation by the 115 keV electrons did not produce changes as great as those following irradiation in the 10^{-8} mm Hg ambient.

Figure 4 shows the results of irradiating this same 20 ohm-cm p-Si surface in the 10^{-5} mm Hg vacuum of the Van de Graaff machine. Prior to exposure to the electrons the surface was washed successively in acetone and methanol. Curve a) represents the results of the first run; curve b), the results of the second and subsequent runs. Note that the actual values of V_{sc} are not directly related to V_{sc} in the Vac-Ion system because the geometry of the second system leads to somewhat different light intensities at the sample surface. However, there is a striking difference between the response of the surface to irradiation in this organic-vapor contaminated ambient and its behavior in the organic vapor free ambient provided by the Vac-Ion system. An additional contrast is the absence of any great difference between the first and subsequent irradiations. Furthermore, the "annealing" or recovery of the surface is more substantial and more rapid than in the organic-vapor free vacuum. These results are essentially the same as those reported in our last semiannual report, except that the changes are not as great. In the earlier work, the current of bombarding electrons was greater (about $5\mu A/cm^2$) and the integrated flux required to achieve saturation was greater (about 5000μ coul/cm^2).

Figures 5, 6 and 7 show the results of a similar set of irradiations of 20 ohm-cm, n-Si. Here again the first irradiation in the 10^{-8} mm Hg Vac-Ion vacuum leads to a large change (Figure 5a) by a factor of 3 whereas the second and subsequent irradiations (Figure 5b) did not result in much change. Furthermore, the amount of annealing which occurred during the 20 hour rest between irradiations is negligible. When dry N_2 was admitted to a pressure of 5μ (Figure 6a), the response dropped to about 0.7 of its value in the 10^{-8} mm Hg vacuum. Irradiation led to a gradual increase of V_{sc} until it saturated at about the same value as it had in the high vacuum.

Irradiation in the Van de Graaff vacuum (10^{-5} mm Hg) again led to a dramatic difference in behavior as shown in Figure 7. The response decayed substantially

(by a factor of 10) after 1000μ coul/cm^2 and had not as yet saturated. During the 20 hour rest, the surface recovered virtually all of its response and the second irradiation did not cause as great a decrease in V_{sc}.

Figures 8, 9 and 10 present the same sequence of irradiations for a 1 ohm-cm, n-Si surface. In this case, irradiation produced an increase in V_{sc} (a decrease in s) in all three ambients. The smallest change (about 20%) occurred in the high vacuum (10^{-8} mm Hg) while the largest change (a factor of 6) occurred in the Van de Graaff vacuum. The saturation value of V_{sc} in the organic-vapor free vacuum was different in the high vacuum case (Figure 8) than in the case of irradiation in a dry nitrogen ambient (Figure 9).

Figures 11, 12 and 13 show the results of the same sequence of irradiations for a 50 ohm-cm, n-Si surface. In all three ambients V_{sc} first increased and after attaining a maximum which was about a factor of 2 greater than its initial value it decreased until saturation had set in after about 1000μ coul/cm^2. In this case again the recovery during the rest period is greatest for the sample irradiated in the Van de Graaff vacuum.

VI. Discussion of Results

Probably the most important result of the irradiation in the organic-vapor free vacua is the high degree of stability with time and exposure to flux which is achieved for the silicon surfaces studied here after the initial irradiation. The stable value attained after exposure to about 10^{15} electrons/cm^2 was higher than the initial value of a fresh surface in all cases except the 50 ohm-cm n-Si case. This result suggests that it is possible to stabilize the surface recombination velocity of silicon devices sealed in a high vacuum by continuously exposing them to ionizing radiation like that provided by radioisotopes. Furthermore for most resistivities the saturation value of s is lower than in the pre-irradiated state so that the operating characteristics of the devices would be superior to those of devices not subjected to this low level irradiation. The experiments indicate that about 10^{15} electrons cm^2 are needed to induce this stabilized surface. Since 1 curie corresponds to 3 x 10^{10} disintegrations/sec, this means that if the device is exposed to a curie of say tritium for 10^5 sec (about 2 days) it will have attained its stable value.

The stability achieved by the surface in the high vacuum environment also means that studies of bulk damage could proceed in this high vacuum with relatively little interference from the surface effects of radiation. In particular, the technique based on the photovoltaic effect associated with strongly absorbed light could be adapted to the study of radiation damage thresholds and especially orientation effects.

Presumably the reason for this stable state in the high vacuum is the removal from the environs of the surface of substances whose presence on the surface causes large changes in s. This means that the residual gases in an organic-vapor free vacuum are not very effective in controlling s. This conclusion is supported by the fact that the addition of N_2 to the ambient even at a pressure of 10^{-3} mm Hg did not have much effect on the stability attained after relatively low intensity

irradiations and by the fact that irradiation in the Van de Graaff vacuum led to more rapid changes in s.

Since the surfaces are not atomically clean, it is reasonable to suppose that the initial irradiation causes a redistribution of adsorbed atoms on the surface and that subsequent irradiations do not have much effect on this new distribution. As is well known, the surface recombination velocity can change either because the surface potential ψ_s has changed or because the number of recombination centers has changed. Changes in surface potential alter the position of the Fermi level within surface space charge layer. This leads to a change in the occuppancy of the "fast states" at the interface between the oxide and the main body of the crystal. These fast states are the recombination sites. Irradiation can change the number and nature of these recombination states, but it can also change the surface potential by changing the population of adsorbed atoms. It is difficult to distinguish between changes in surface potential and changes in the numbers or nature of recombination centers on the basis of the experiments performed to date. In order to make this distinction, it will be necessary to perform some experiments in which we will alter ψ_s by applying a field in the vicinity of the surface. If ψ_s is varied for surfaces before and after irradiation, comparison of s vs ψ_s curves for the two cases will establish whether the recombination center population was changed by the irradiation or whether the changes can be explained entirely in terms of ψ_s changes.

As regards the experiments in the Van de Graaff vacuum, they demonstrate that the residual gases play an important role in determining s. One obvious difference in the two ambients is the presence in the Van de Graaff vacuum of residues of organic vapors associated with neoprene gaskets and diffusion pump oil. These results suggest that extrapolations based on irradiation experiments involving surface effects performed in such vacua to the behavior of devices in the vacuum of outer space can lead to erroneous conclusions.

VII. Conclusions

1. There are essential differences in the electron bombardment induced changes in surface recombination velocity of silicon surfaces irradiated in organic-vapor contaminated ambients and in ambients from which organic vapors have been excluded. Dry nitrogen added to an organic-vapor free ambient does not cause any significant change in the surface radiation effects even though the pressure is a few microns.

2. The surfaces of all the silicon specimens examined in the course of this investigation changed in such a way as to decrease surface recombination velocity s. These materials included 1, 20 and 50 ohm-cm n-Si and 20 ohm-cm p-Si surfaces.

3. There was a substantial difference between the electron flux dependence of s during the first irradiation and all subsequent irradiations in the high vacuum, organic-vapor free ambient. This was true even though the samples had been heated to about 100°C in a pre-pumping bake-out. A possible explanation for this behavior is that the first irradiation produces certain irreversible changes in the distribution of atoms adsorbed on the surface and that the new destribution is relatively stable in an organic-vapor free ambient.

4. The irradiation produced changes in s anneal very slowly in organic-vapor free vacua. Thus irradiation in such vacua led to stabilization of s.

VIII. Future Plans

During the remaining period of this investigation, we shall irradiate, in the organic-vapor free high vacuum, surfaces on other silicon resistivities. In particular, we shall study the effect of irradiation on the diffused faces of silicon n/p and p/n surfaces in this ambient. We also hope to compare the effects of radiation on a Ge surface in the organic vapor-free and organic vapor contaminated vacua. If time permits, we shall study the dependence of surface recombination velocity on surface potential for Si in order to distinguish between radiation induced changes in ψ_s and in the recombination center population.

References

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2. J. J. Loferski, W. Giriat, and I. Kasai, Photovoltaic Effect and Utilization of Photovoltaic Cells, Second Semiannual Report on NASA Grant NGR-40-002-026, June, 1966.

3. J. J. Loferski, I. Kasai, W. Giriat, Photovoltaic Effect and Utilization of Cells, Third Semiannual Report on NASA Grant NGR-40-002-026, December, 1966.

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Figure Titles

Figure 1: Schematic diagram of the chamber used for irradiation of samples in the Vac Ion vacuum

Figure 2: The photovoltaic voltage across a "shorting resistor" of 100Ω V_{sc} in arbitrary units as a function of 115 keV electron flux for the surface of 20 ohm-cm p-Si. The surface is illuminated by monochromatic light of λ = 3650Å. The sample was in an organic-vapor free vacuum of 10^{-8} mm Hg produced by a Vac-Ion Pump. Curve (a) corresponds to the first run on a freshly cleaned surface. Curve (b) corresponds to a second run taken after the cell rested in vacuum for about 20 hours. Subsequent runs yielded curves similar to curve (b).

Figure 3: V_{sc} vs ϕ (115 keV electrons) for surface of 20 ohm-cm p-Si irradiated in a dry nitrogen, organic-vapor free ambient ($p \sim 5 \times 10^{-3}$ mm Hg curve a and $p \sim 3 \times 10^{-2}$ mm Hg curve b)

Figure 4: V_{sc} vs ϕ (115 keV electrons) for the surface of 20 ohm-cm p-Si irradiated in the vacuum provided by the oil diffusion pumps and cold traps of the Van de Graaff pumping system. Curve (a) corresponds to the first run on a clean surface; curve (b) to the second and subsequent runs.

Figure 5: Same as Figure 2 except that the silicon is n-type, ρ = 20 ohm-cm.

Figure 6: Same as Figure 4 except that the silicon is n-type, ρ = 20 ohm-cm.

Figure 7: Same as Figure 4 except that silicon is n-type, ρ = 20 ohm-cm.

Figure 8: Same as Figure 2 except that silicon is n-type, ρ = 1 ohm-cm.

Figure 9: Same as Figure 3 except that silicon is n-type, ρ = 1 ohm-cm.

Figure 10: Same as Figure 4, except that silicon is n-type, ρ = 1 ohm-cm.

Figure 11: Same as Figure 2 except that silicon is n-type, ρ = 50 ohm-cm.

Figure 12: Same as Figure 3 except that silicon is n-type, ρ = 50 ohm-cm.

Figure 13: Same as Figure 4 except that silicon is n-type, ρ = 50 ohm-cm.

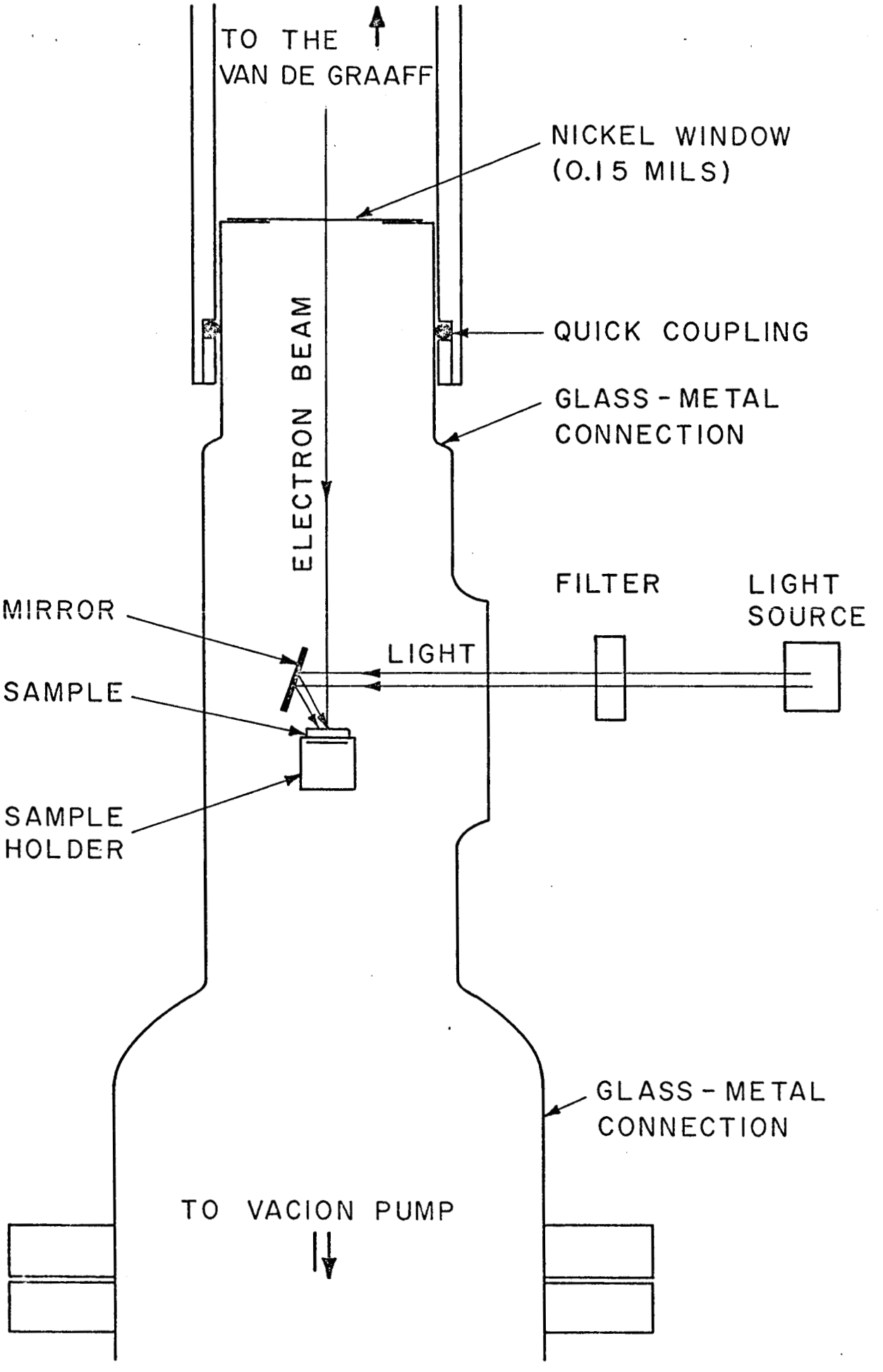
TO THE
VAN DE GRAAFF
NICKEL WINDOW
(0.15 MILS)
QUICK COUPLING
GLASS - METAL
CONNECTION
ELECTRON BEAM
FILTER
LIGHT
SOURCE
MIRROR
LIGHT
SAMPLE
SAMPLE
HOLDER
GLASS - METAL
CONNECTION
TO VACION PUMP

FIG. 1

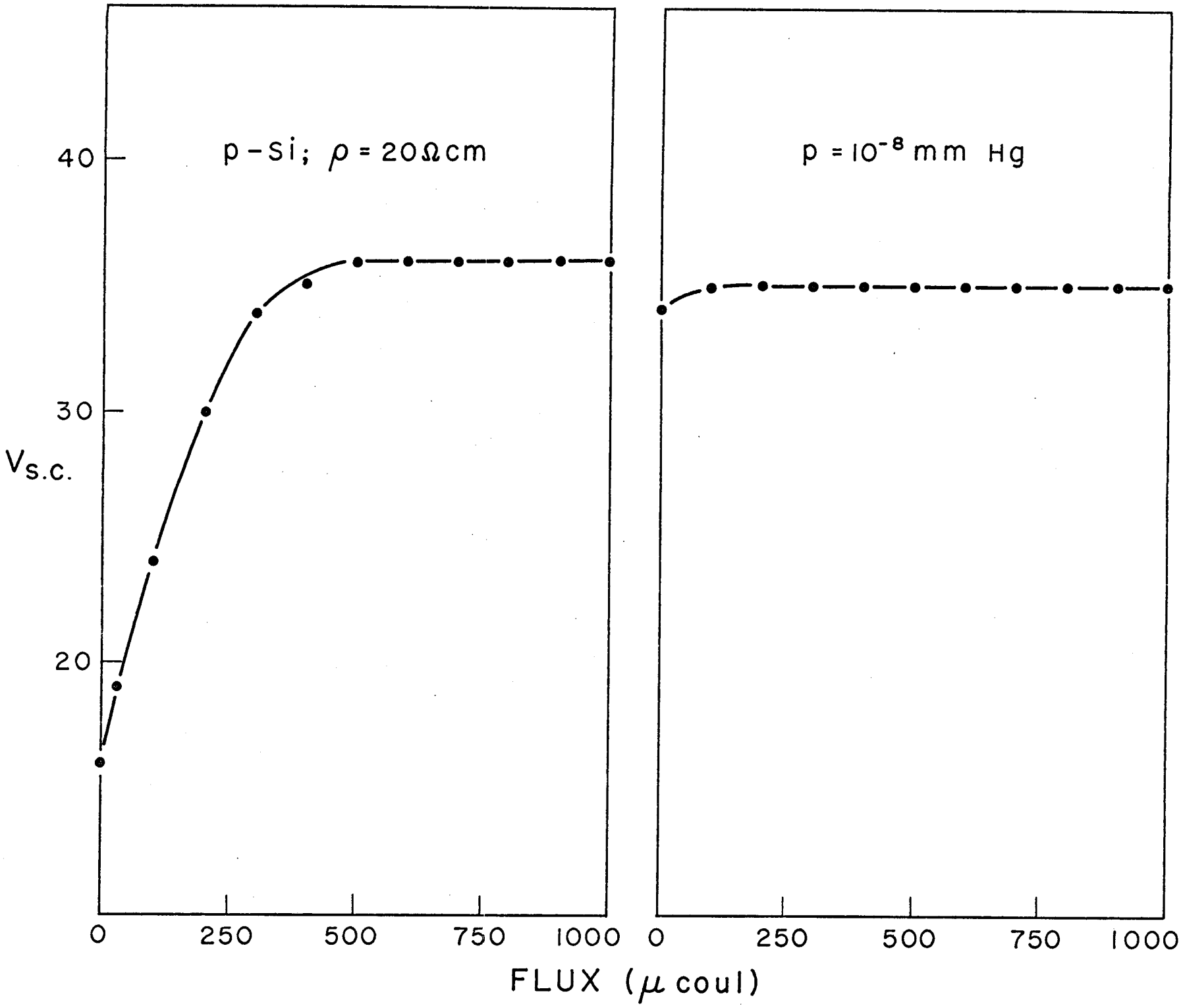
p - Si; ρ = 20Ωcm
p = 10⁻⁸ mm Hg
40
30
20
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 2

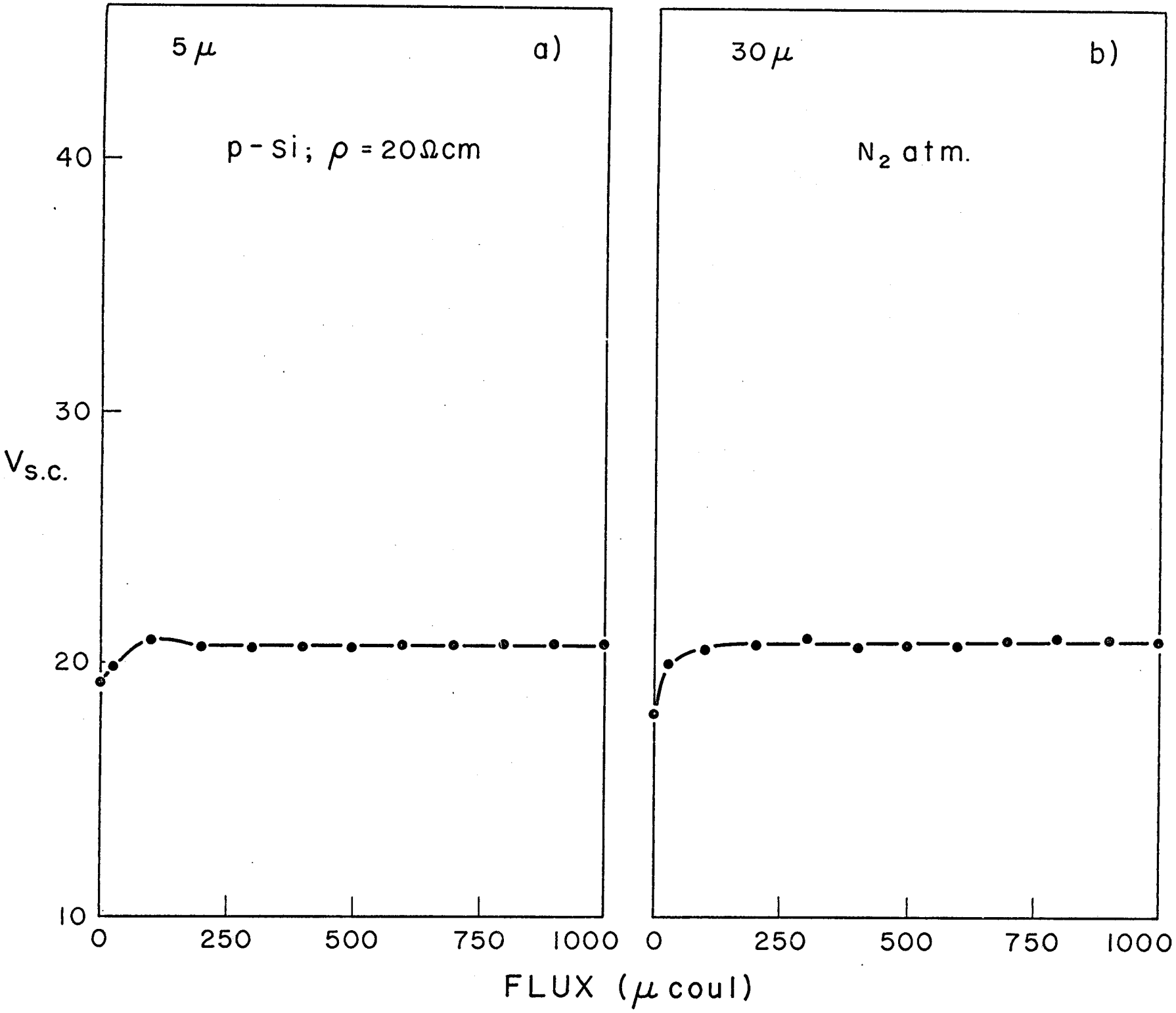
5 μ
a)
p - Si ; ρ = 20Ωcm
30 μ
b)
N2 atm.
40
30
20
10
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 3

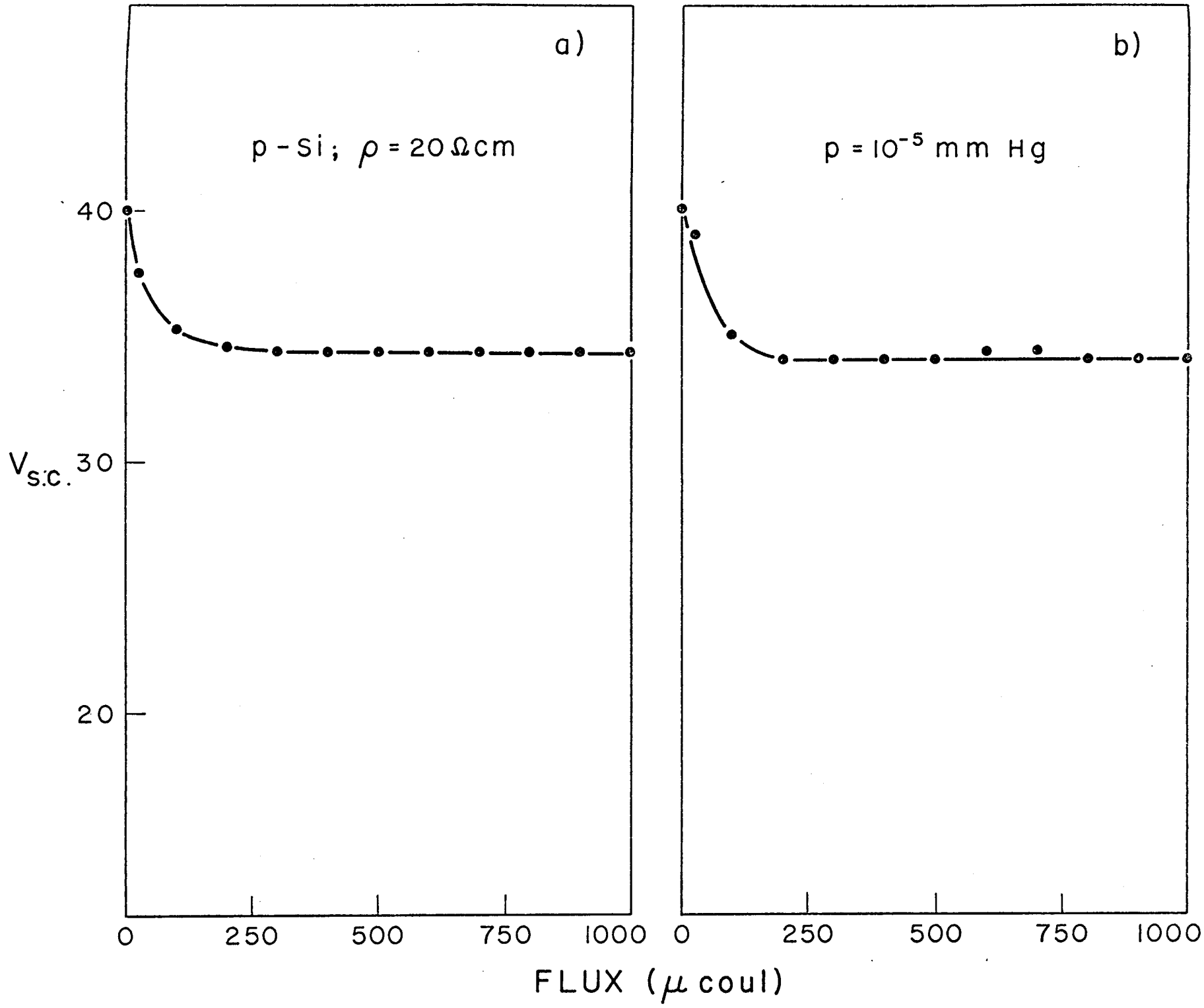
a)
p - Si; ρ = 20 Ωcm
b)
p = 10⁻⁵ mm Hg
40
30
20
V s.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 4

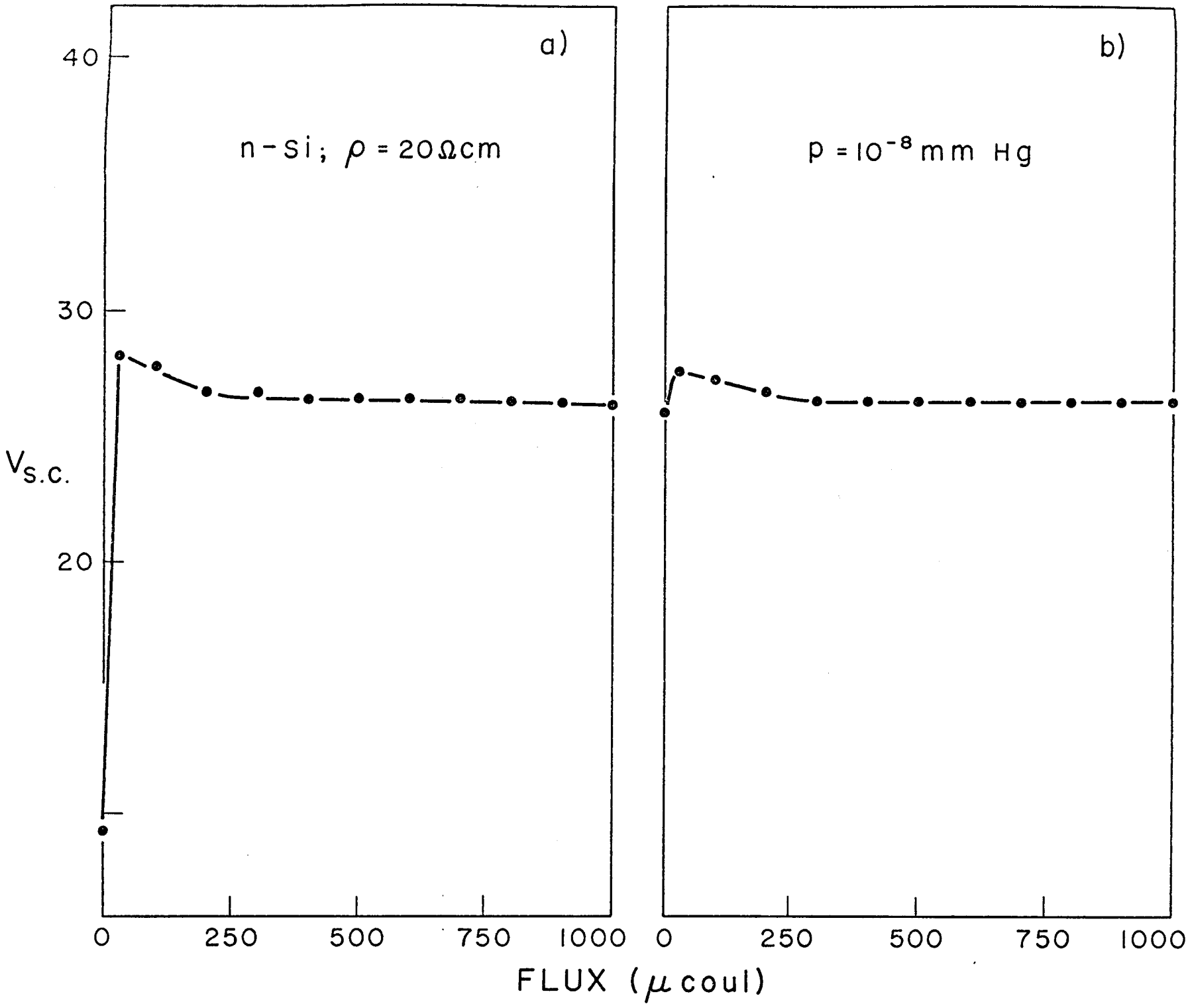
a)
b)
n-Si; ρ = 20Ωcm
p = 10⁻⁸ mm Hg
40
30
20
$V_{s.c.}$
0
250
500
750
1000
0
250
500
750
1000
FLUX (μcoul)

FIG. 5

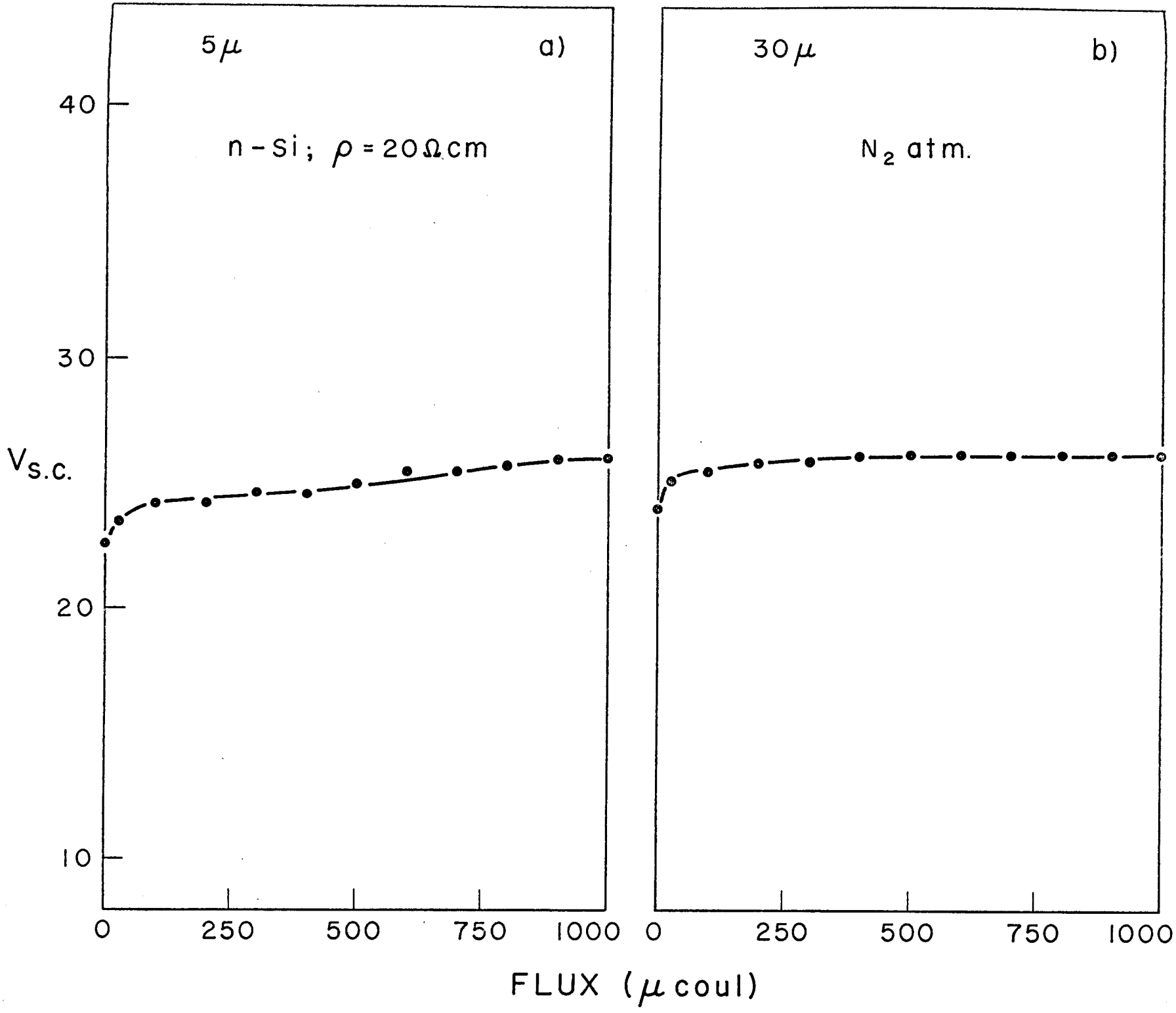
5μ
a)
30μ
b)
40
30
20
10
n-Si; ρ = 20Ω cm
N2 atm.
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 6

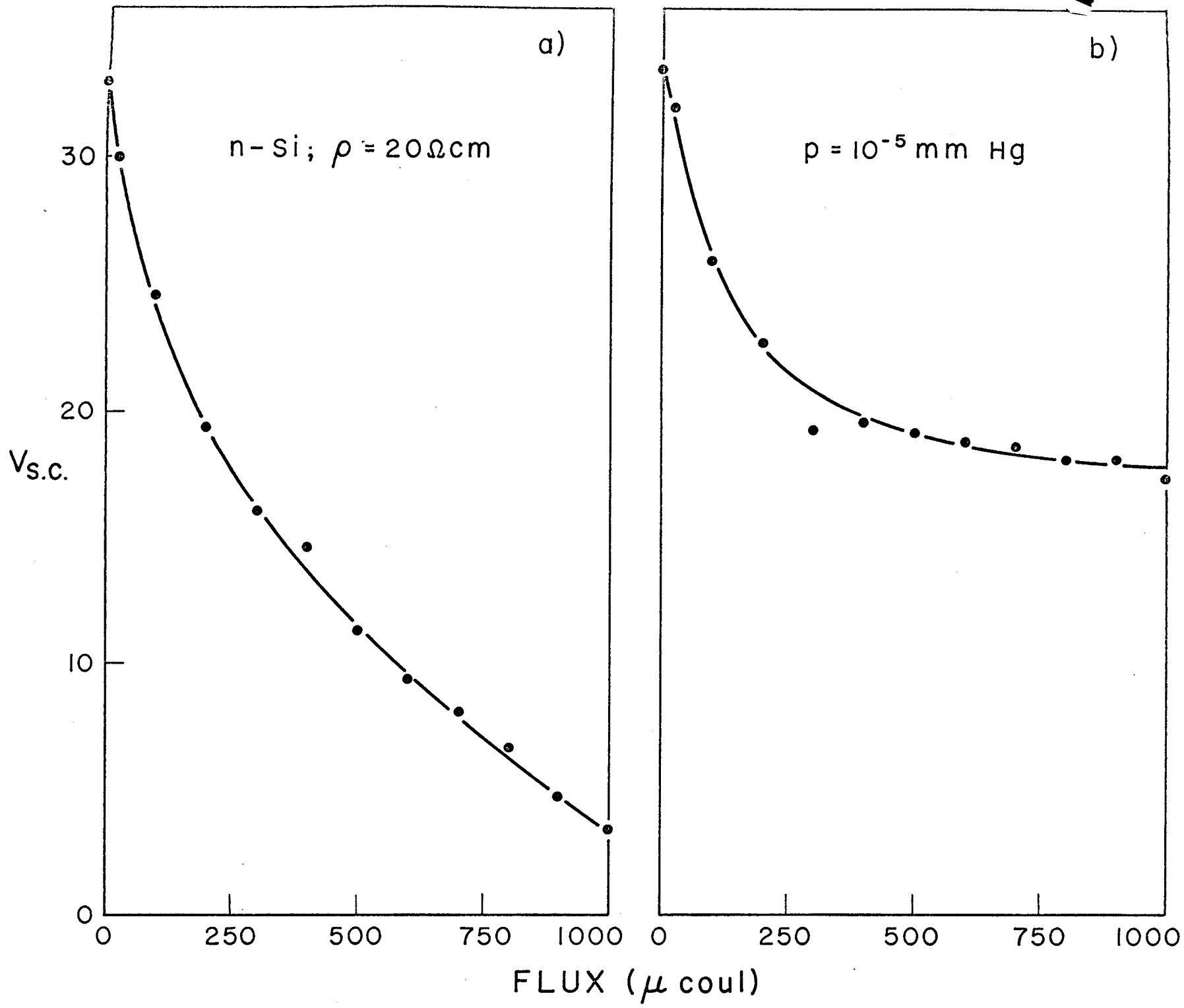
a)
b)
n-Si; ρ = 20Ωcm
p = 10⁻⁵ mm Hg
30
20
10
0
Vs.c.
0
250
500
750
1000
FLUX (μ coul)

FIG. 7

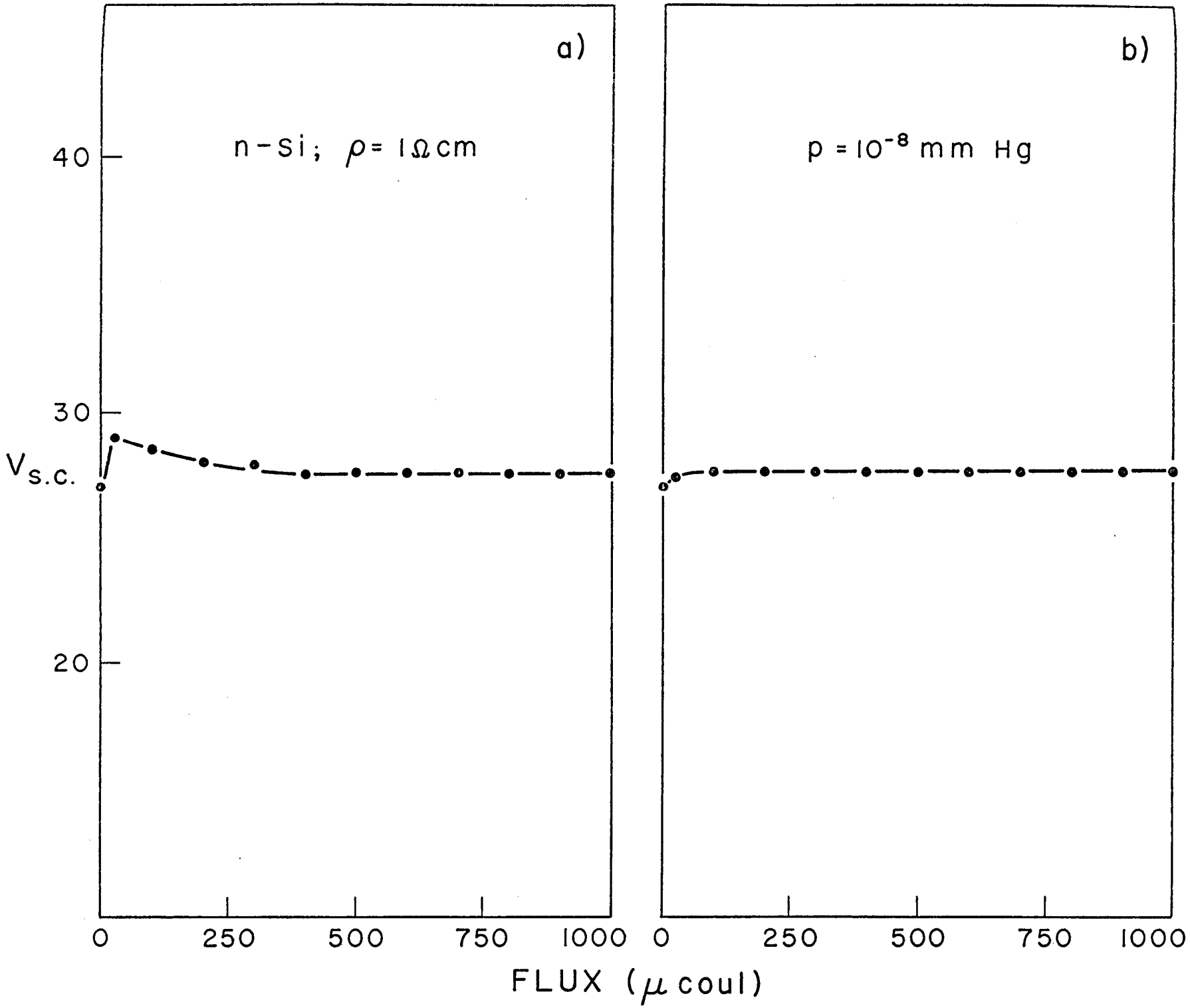
a)
b)
n-Si; ρ = 1Ω cm
p = 10⁻⁸ mm Hg
40
30
20
V s.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 8

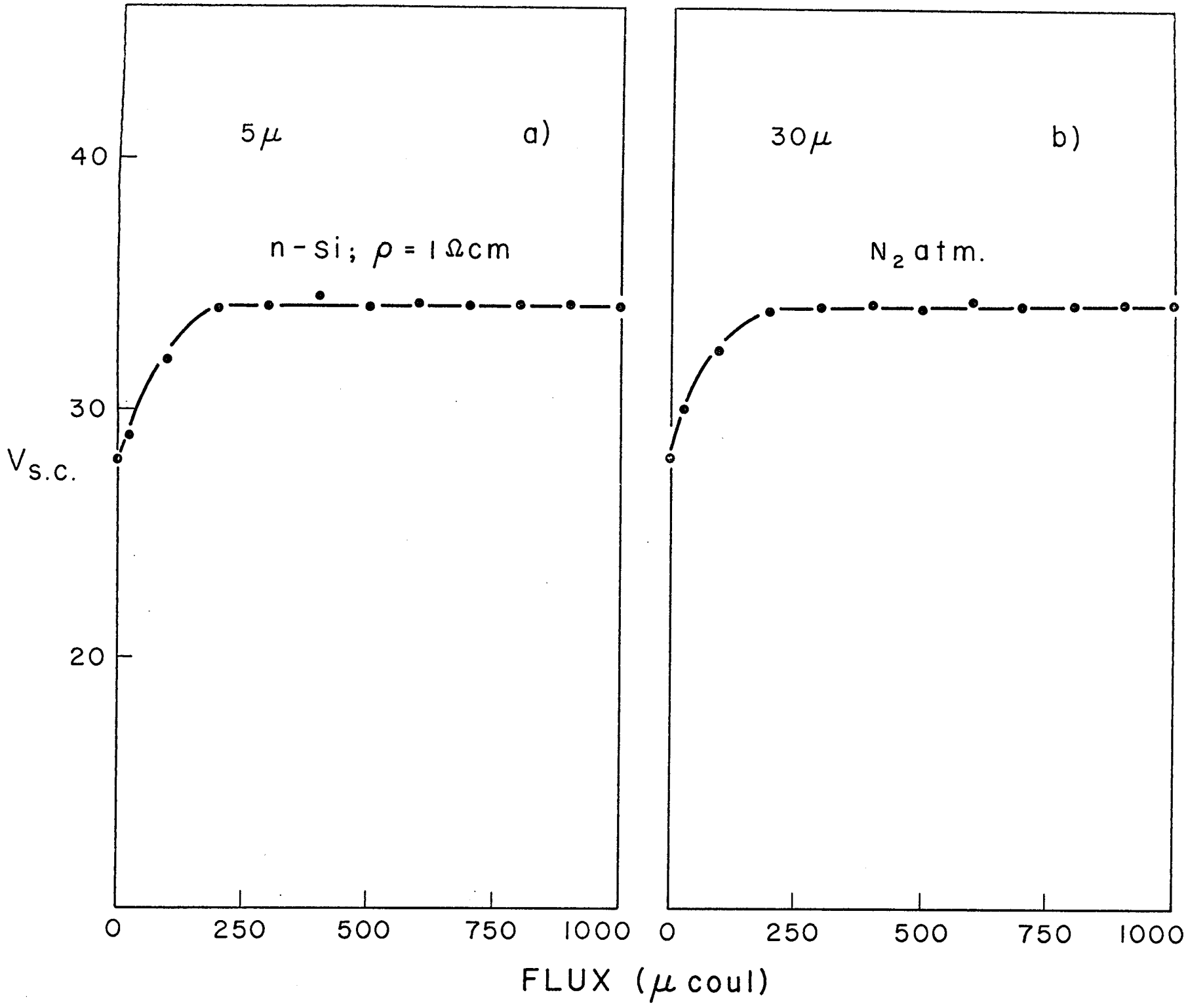
5μ
a)
30μ
b)
40
30
20
n-Si; ρ = 1 Ωcm
N2 atm.
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 9

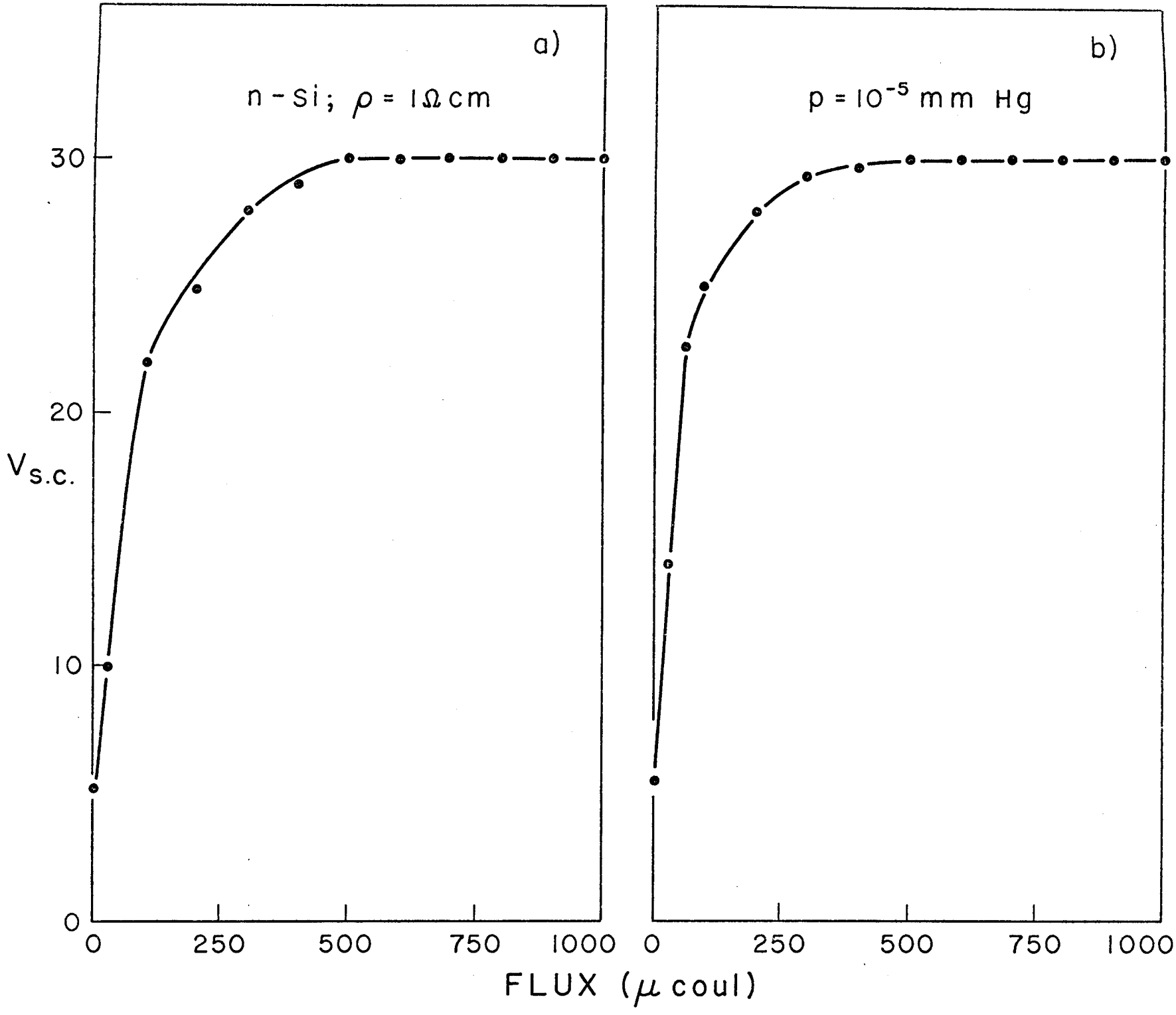
a)
n - Si; ρ = 1Ω cm
b)
p = 10⁻⁵ mm Hg
30
20
10
0
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 10

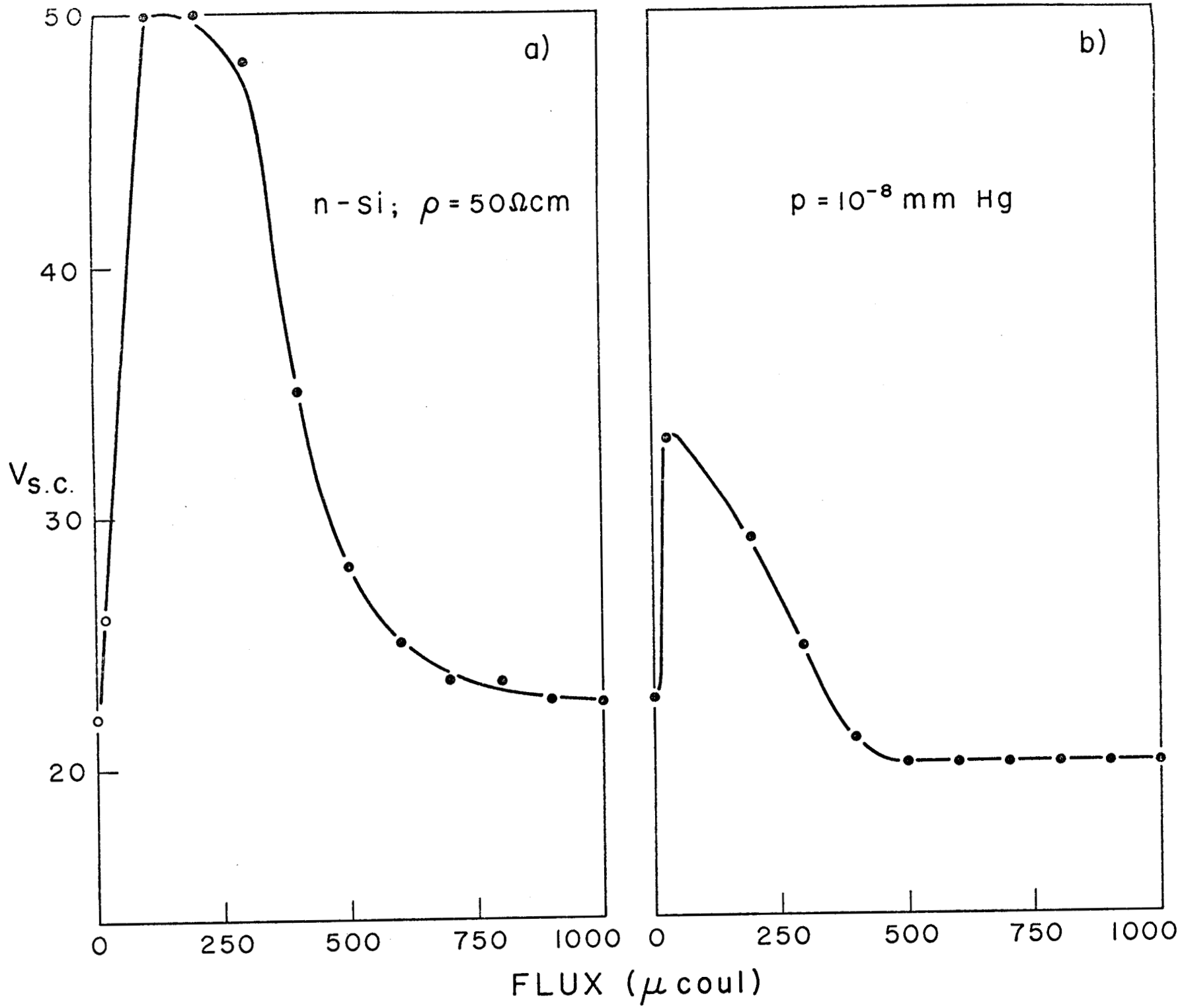
50
40
30
20
$V_{s.c.}$
a)
n-Si; $\rho = 50\Omega cm$
b)
$p = 10^{-8}$ mm Hg
0
250
500
750
1000
0
250
500
750
1000
FLUX (μcoul)

FIG. 11

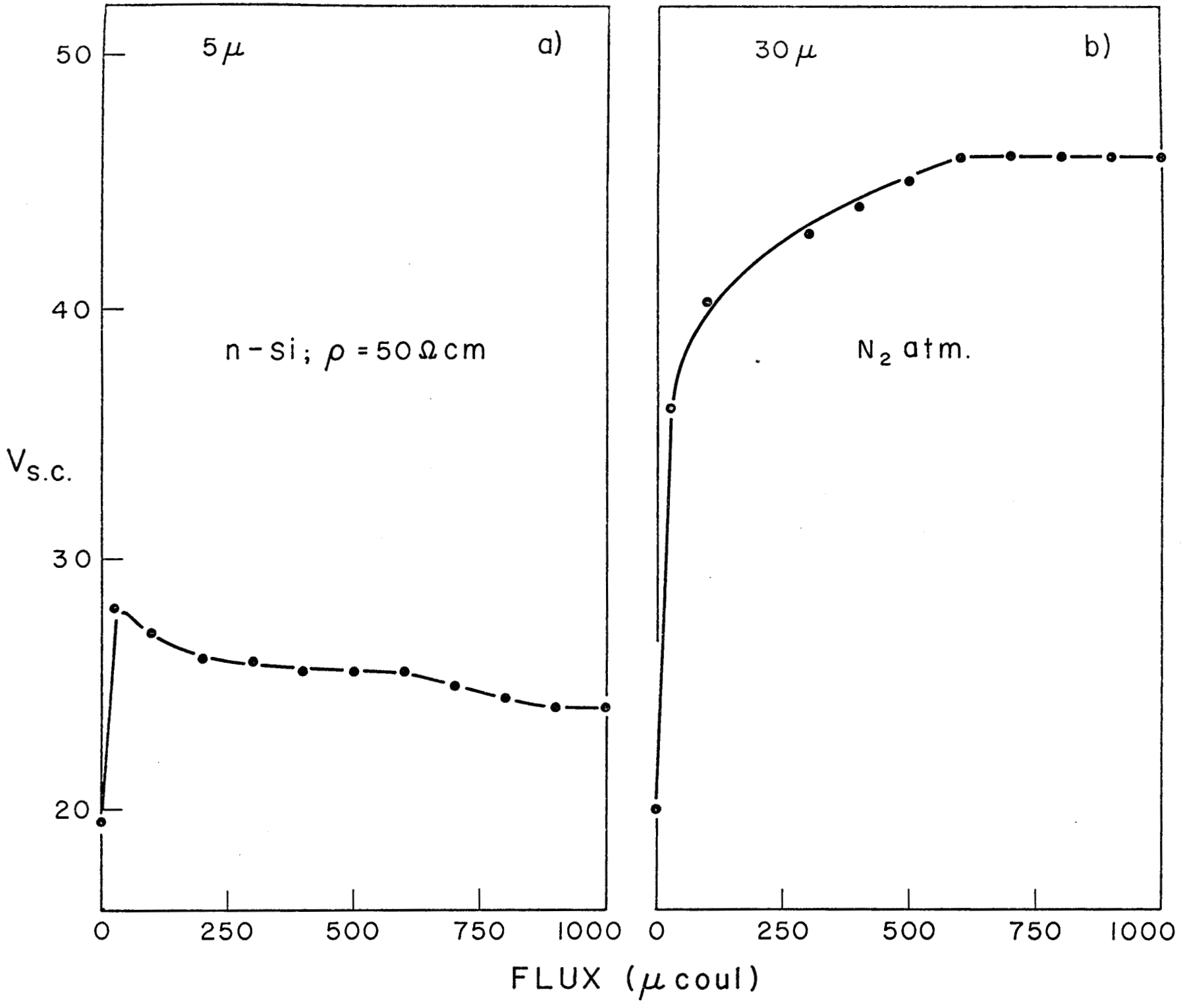
5μ
a)
30μ
b)
50
40
30
20
n-Si; ρ = 50 Ω cm
N2 atm.
Vs.c.
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 12

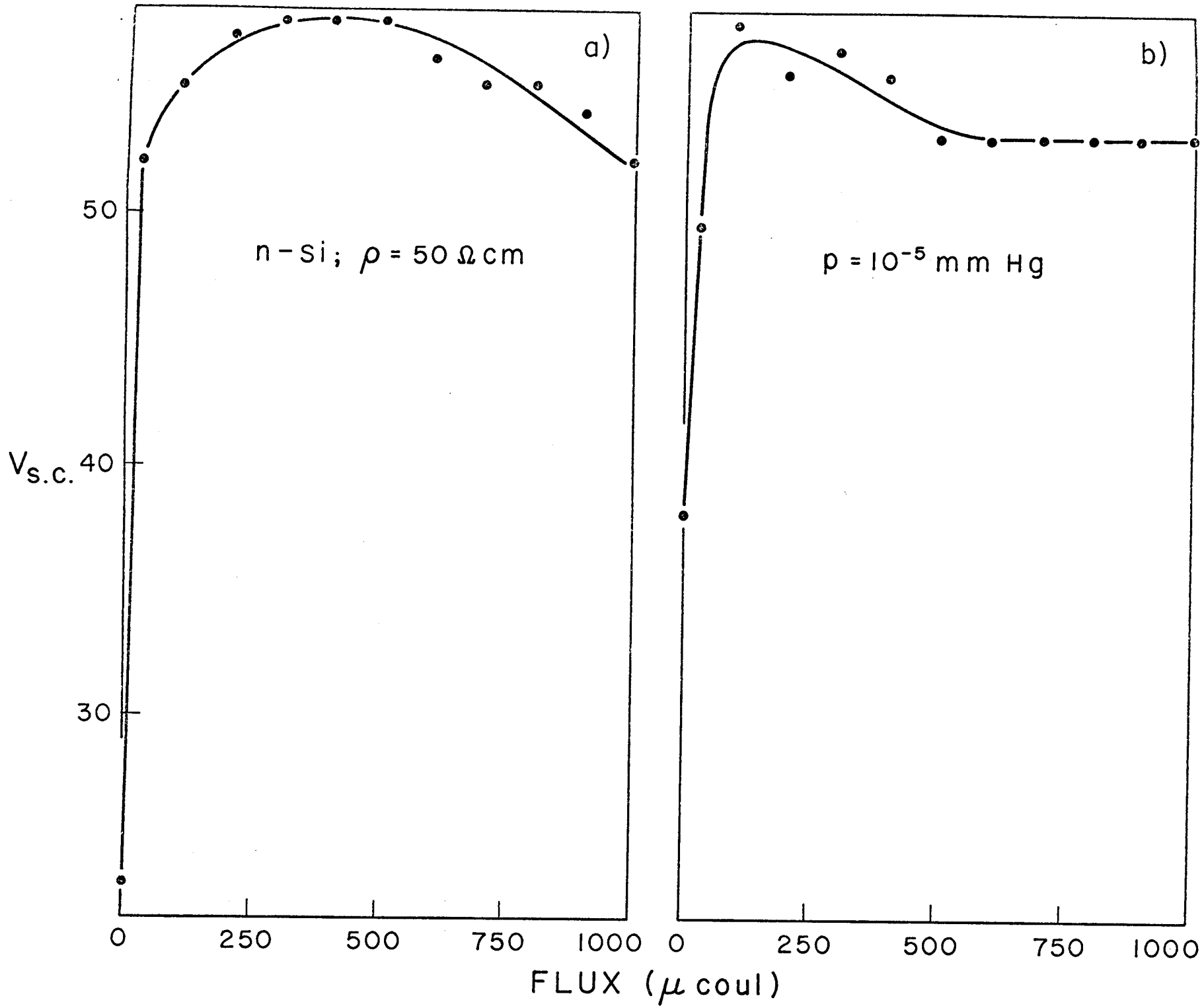
a)
b)
n-Si; ρ = 50 Ω cm
p = 10⁻⁵ mm Hg
50
40
30
$V_{s.c.}$
0
250
500
750
1000
0
250
500
750
1000
FLUX (μ coul)

FIG. 13